POTENTIALLY HAZARDOUS TRACE ELEMENTS IN KENTUCKY COALS

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INTRODUCTION

The minor and major trace elemental content of coal is of great interest because of the potentially hazardous impact on human health and the environment resulting from their release during coal combustion. Of the one billion tons of coal mined annually in the United States, 85-90% is consumed by coal-fired power plants.[1] Potentially toxic elements present at concentrations as low as a few μg/g can be released in large quantities from combustion of this magnitude.

The 1990 Amendments to the Clean Air Act listed 12 elements found in coal as being potentially subject to control: Sb, As, Be, Cl, Cd, Co, Cr, Pb, Hg, Mn, Ni, and Se. In this study the partitioning of these and other elements during coal combustion and advanced cleaning processes has been investigated. Elemental concentrations were measured in the fractions obtained before and after combustion or cleaning using external beam particle induced X-ray emission (PIXE). PIXE is a rapid, instrumental technique that, in principle, is capable of analyzing all elements from sodium through uranium without chemical interference effects. In practice more than 20 elements are routinely determined with sensitivities as low as 1 μg/g.

EXPERIMENTAL

Sample Preparation

Combustion studies. Samples of feed coal, fly ash, and bottom ash were collected from two western Kentucky coal-fired power plants (Plants A and B). Each sample was ground to -225 mesh and dried at 105°C overnight. The ash samples were mixed with dried, high-purity graphite to obtain ~30% by weight of ash. Each coal and ash/graphite sample was pressed into a 1 mm x 19 mm pellet.

Coal cleaning studies. A sample of run of mine coal from the Kentucky #9 seam was collected at the mine site, and split into subsamples as needed. Each subsample was ground to -325 mesh and a 5% (w/v) slurry was prepared. The slurry was subjected to Denver floatation, and the float fraction was further subjected to hydrothermal leaching using either a NaOH or HNO$_3$ solution. The duration, temperature, and pressure of the leaching process were varied to ascertain their influence, if any, on the removal of trace elements. The clean coal was dried at 50°C overnight, and pressed into a pellet as described above.

Experimental Setup

The samples were irradiated with an external 1.6 MeV and 2.1 MeV proton beam. The beam, at an angle of 23° relative to the sample surface, was swept over the target to irradiate a 16 mm diameter area. The sample chamber was flushed with helium at atmospheric pressure to reduce sample heating and charging. X-rays were detected with a Si(Li) detector (FWHM resolution of 160 eV at 5.90 keV) placed at an angle of 45° relative to the incident beam. The irradiation time for each sample was 15 minutes. A typical PIXE spectrum of a coal sample is shown in Figure 1. Similar spectra are obtained from the analysis of fly ash and bottom ash. Data analyses were performed using the GUPIX[2] PC-based software.

RESULTS & DISCUSSION

Combustion studies. Enrichment factors, shown in Figures 2 and 3, are used to illustrate the partitioning behavior of elements during coal combustion. The enrichment factor, EF, for element X is given by:

$$EF = \frac{[X]_{ash}/[X]_{feed\ coal}}{[Al]_{ash}/[Al]_{feed\ coal}}$$

The ratio of the concentration of X in the ash and feed coal is calculated relative to the ratio of the concentration of Al in the same
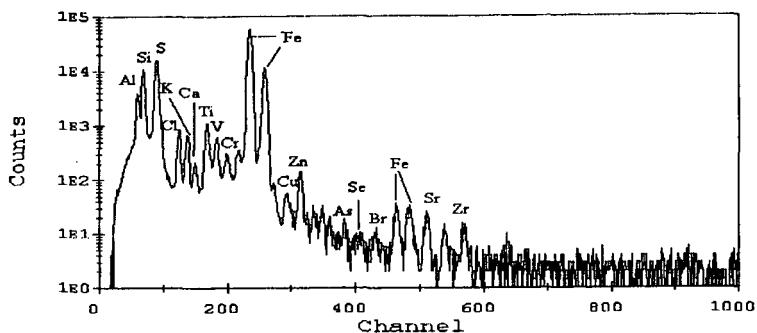
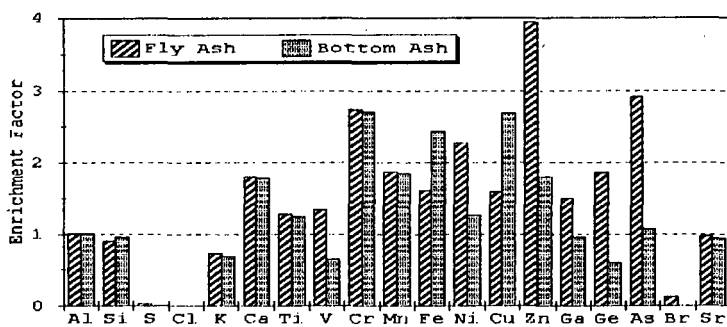Figure 1. Typical PIXE spectrum of coal.

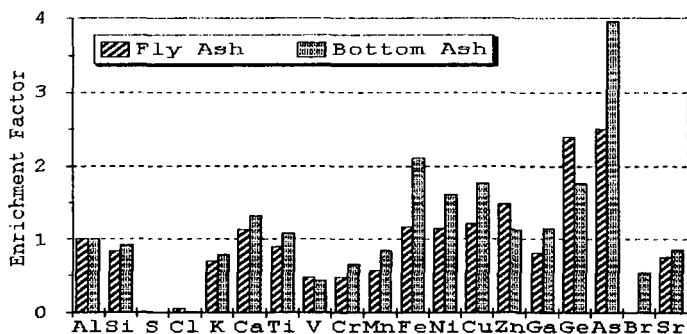Figure 2. Enrichment factors for Plant A.

Figure 3. Enrichment factors for Plant B.

ash and feed coal samples because Al is known to partition equally between the fly ash and bottom ash. The partitioning of elements observed in Plant A is consistent with accepted partitioning behavior.

However, different results were obtained from Plant B samples. Figure 3 illustrates that the majority of the elements were more enriched in the bottom ash than in the fly ash: Ca, Ti, Cr, Mn, Fe, Ni, Cu, Ga, As, and Br. This unusual enrichment in the bottom ash was thought to be due to the addition of tailings from the coal cleaning processes to the bottom ash. Plant operators later confirmed the use of this practice at the plant.

Coal cleaning studies. Concentration factors were used to evaluate the effectiveness of the hydrothermal leaching coal cleaning process. The concentration factor, CF, for element X is given by:

$$CF = \frac{[X]_{clean\ coal\ (hydrothermal\ leaching)}}{[X]_{float\ fraction\ (Denver\ floatation)}}$$

Thus, a CF < 1 indicates a reduction in the concentration of that element as a result of hydrothermal leaching. A comparison of the CFs obtained using NaOH and HNO_3 as the chemical leaching agents is shown in Figure 4. The increase observed in the concentration of some elements (i.e. CF > 1) could be the result of these elements being leached from reactor components. The increase may also be due to a contaminated leaching solution. It should be noted, however, that the elements whose concentration did increase are not of significant environmental concern.

HNO_3 was more effective than NaOH in reducing elemental concentrations for all elements except V and Ga. When HNO_3 was the leaching agent most elements were removed very efficiently (CF < 0.5). The degree to which elements are removed by coal cleaning processes depends to a great extent on their mode of occurrence or chemical association in the coal. Although the exact composition can vary greatly from one coal to the next, generalizations have been made concerning common modes of occurrence for trace elements in coal.[3,4,5] Mg, Ca, Mn, and Sr have a carbonate association in some coals. This would explain their efficient removal since the solubilities of carbonates increase in acidic solutions. Elements known to have an association with pyrite, Fe, S, As, Zn, Ni, and Ga, all show a significant decrease in concentration. Similarly, a considerable reduction in elements known to be strongly associated with silicates, Si, Al, Mg, and K, was observed. The reduction in Cl and Br concentrations by both NaOH and HNO_3 treatment could indicate they are present as soluble salts.

Elements thought to have a significant organic association were removed less efficiently by HNO_3. In these samples, those elements were
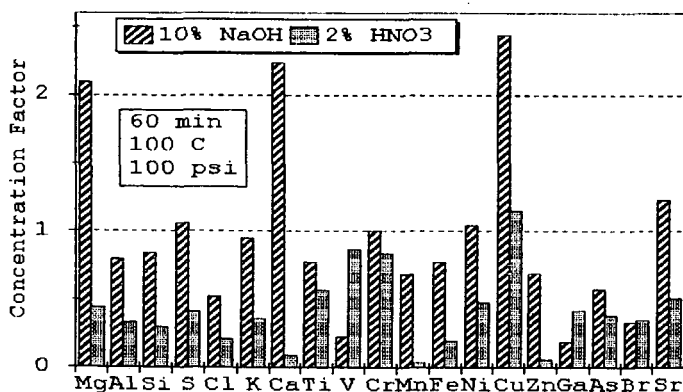

Figure 4. Concentration factors for NaOH and HNO_3.

V, Cr, Ti, and Cu. X-ray absorption fine structure spectroscopy of Kentucky #9 coal has indicated a partial organic association for V, Cr, and Ti. Although the association of Cu has not been determined in these samples, Cu is known to have partial organic associations in other coals.

The effect of other variables in the hydrothermal leaching process are illustrated in Figures 5-7. Increases in the duration, pressure and temperature of the hydrothermal leaching process showed essentially no improvement in the reduction of elemental concentrations for some elements and only slight improvements for others. Thus, it appears these variables have minimal impact on the effectiveness of this coal cleaning process.

SUMMARY

The partitioning of elements during coal combustion is influenced by the mode of occurrence of the elements in the feed coal, boiler characteristics, and the volatility of the species present. Therefore it is not unusual to observe differences in the partitioning of elements
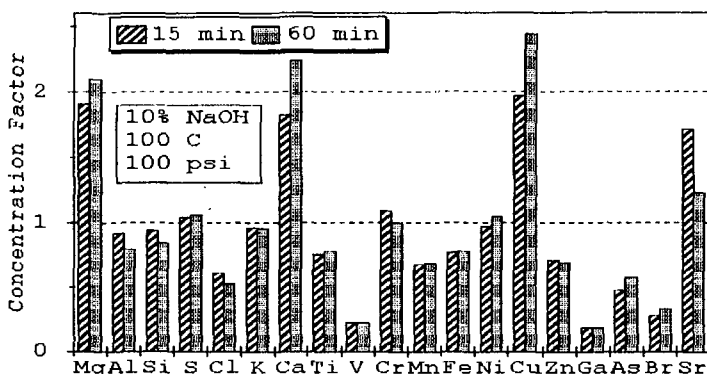
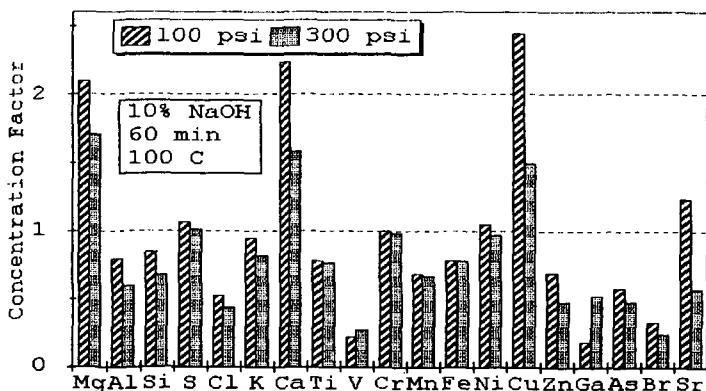Figure 5. Concentration factors for different leaching time periods.

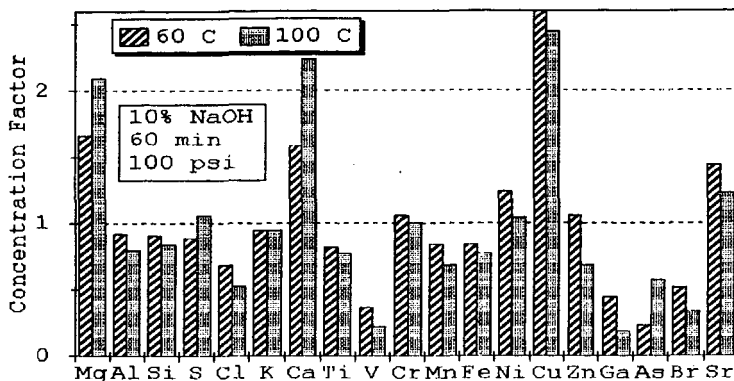Figure 6. Concentration factors for different pressures.

Figure 7. Concentration factors for different temperatures.

at different coal-fired power plants using different feed coal. Nevertheless, the differences observed in this study are more likely caused by the addition of wastes from coal cleaning processes to the bottom ash of Plant B.

The variable with the greatest impact on hydrothermal leaching appears to be the leaching chemical itself. A significant reduction in the concentration of many elements was observed with the use of HNO_3 as the leaching agent. Present data suggests other variables in the process have only slight impact on the removal of hazardous elements in coal. Work is ongoing to optimize the overall system to obtain the lowest possible elemental concentrations.

Of the 12 "air toxics" listed in the 1990 Clean Air Act Amendments Cl, Cr, Mn, Ni, and As were analyzed in this work. The remaining seven elements not analyzed were present at levels below the sensitivity of our experimental system, however future work on these samples will include analyzing for these elements using neutron activation analysis.

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